J. of Supercritical Fluids 127 (2017) 229–246

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Review

Polymer materials for electrochemical applications: Processing in supercritical fluids

Mikhail S. Kondratenko[a], Igor V. Elmanovich[a,b], Marat O. Gallyamov[a,b,*]

[a] *Faculty of Physics, M.V. Lomonosov Moscow State University, Leninskie Gory 1-2, GSP-1, Moscow 119991, Russian Federation*
[b] *A.N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, GSP-1, Moscow 119991, Russian Federation*

ARTICLE INFO

Article history:
Received 11 October 2016
Received in revised form 15 March 2017
Accepted 15 March 2017
Available online 18 March 2017

Keywords:
Supercritical fluid
Conducting polymer
Membrane
Porous matrix
Composite
Nafion

ABSTRACT

In this review we discuss the usage of supercritical fluids for processing (synthesis, modification, forming, etc.) of polymeric materials for electrochemical applications. Our primary focus is on the literature that reveals the benefits of this approach for processing electronically conductive polymers. Recent literature on ion-conductive polymers is also analyzed. The achieved advances as well as remaining questions and challenges still to be faced are generally outlined.

Contents

---

[*] Corresponding author at: M.V. Lomonosov Moscow State University, Faculty of Physics, Leninskie Gory 1-2, GSP-1, Moscow 119991, Russian Federation.
E-mail address: glm@spm.phys.msu.ru (M.O. Gallyamov).

http://dx.doi.org/10.1016/j.supflu.2017.03.011
0896-8446/

Nomenclature

AN	Acetonitrile
APS	Ammonium peroxydisulfate
BPO	Benzoyl peroxide
CFC-113	1,1,2-Trichloro-1,2,2-trifluoroethane
DBSA	Dodecylbenzenesulfonic acid
DFHDPA	Dodecafluoroheptyldipropargyl acetate
DFE	Difluoroethane
DMA	Dimethylacetamide
DMFC	Direct methanol fuel cell
DMSO	Dimethyl sulfoxide
DVB	Divinylbenzene
EW	Equivalent weight
GO	Graphene oxide
HFC	Hydrofluorocarbon
MWNT	Multi-walled carbon nanotubes
OLED	Organic light-emitting diode
PANI	Polyaniline
PCA	Pyrrole-2-carboxylic acid
PCFTE	Polychlorotrifluoroethylene
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEDOT	Poly(3,4-elthylenedioxythiophene)
PEMFC	Polymer electrolyte membrane fuel cell
PFA	Poly(fluoroalkyl acrylate)
PFFB	Poly[(9-ylidene-{2-tetradecyloxy-5-tetrafluorophthalimidephenyl}fluorenyl-2,7-diyl)-alt-(1,4-phenyl)
PFTE	Perfluoroalkyl ester substituted polythiophene
PTFE	Polytetrafluoroethylene
PLA	Poly(lactide)
PMA	Poly(methyl acrylate)
PMMA	Poly(methyl methacrylate)
PVK	Poly(N-vinylcarbazole)
PPy	Polypyrrole
PS	Polystyrene
PSFTE	Semifluoroalkyl ester substituted polythiophene
PTs	Polythiophenes
PVAc	Poly(vinyl acetate)
PVDF	Poly(vinylidene fluoride)
$scCO_2$	Supercritical carbon dioxide
$scCHF_3$	Supercritical trifluoromethane
SCF	Supercritical fluid
SDS	Sodium dodecyl sulfate
TBAHFP	Tetrabutylammonium hexafluorophosphate
TEM	Transmission electron microscopy
TFODPA	Tridecafluorooctyldipropargyl acetate
THF	Tetrahydrofuran
XRD	X-ray powder diffraction

1. Introduction

Nowadays, electrochemical applications are strongly oriented towards usage of new and advanced polymer materials. Polymers are used in power sources (primary [1] and rechargeable batteries [2], fuel cells [3], redox flow batteries [4], photovoltaic batteries [5,6]), supercapacitors [7], sensors of different types [8,9], electrochromic [10] and other electrochemical devices [11]. Sometimes, even the very word “polymer” is present in the name of modern hi-tech commercial products, such as a well-known Li-polymer battery [12,13]. Additionally, in this regard one can also mention polymer electrolyte membrane fuel cells [14], polymer solar cells [15], smart windows based on polymer dispersed liquid crystal devices [16], which are all on the way to their commercialization. Further, significant part of commercial OLED (organic) displays, polymer light-emitting diodes, is based on high-molecular-weight materials, i.e. polymeric ones [17,18].

In the majority of modern electrochemical applications mentioned above the polymers play an active role: they can be intrinsically electroactive [19], conductive (with electronic and/or ionic conductivity) or even electrocatalytically active [20]. Yet, somewhat more passive role of polymers is also rather important for certain electrochemical applications. For decades, inert porous polymer materials have been successfully serving as convenient and stable matrices-separators for electrolytes [21]. More uniform gel-like polymer matrices for electrolytes are also required for some types of power sources [22]. Further, for quite a long time polymers are widely used as simple binders [23] for an active phase in different power sources, sensors, smart windows, etc. This is due to their adjustable adhesiveness, wettability (including hydrophobicity), permeability, elasticity as well as generally good mechanical properties and processability. Indeed, from a historical viewpoint it is interesting to mention that the first success of fuel cells was related to the pioneer usage of a hydrophobic polymeric binder (Teflon) [24] in FC electrodes in order to develop an important concept of a partially hydrophobized electrode. This problem is specifically relevant particularly to fuel cell electrodes – in distinct from more simple design of electrodes of other types of power sources – due to the necessity to extend a so-called three-phase-boundary (an interface of electrolyte/electrocatalyst/gas reagent phases) [25] on the whole volume of an active (electrocatalytic) material.

Prevention of metal corrosion is another typical electrochemical area, where protective polymeric coatings traditionally play an important role [26]. Yet, it was established that in such applications electroactive polymers (e.g., intrinsically electronically conductive) also behave significantly better as compared to passively protective, i.e., inert ones [27,28].

Rather advanced applications of polymers may be related to the amazing tendency of block copolymers towards self-assembly [29,30]. Highly regular nanostructured mesoporous electrodes and membranes may be created in that way, which widens the arsenal and horizons of electrochemical researchers [31–33].

Block copolymers may help to control spatial organization of electrocatalytic particles in the active phase. Whereas, controlled size, density, regularity, and separation [34] of catalysts particles may affect pathways of electrochemical reactions involved, e.g. intensity of the main reaction (such as, for example, intensity and selectivity of methanol oxidation reaction [35]) and the side reactions (such as, for example, peroxide formation in oxygen reduction reaction [36]). Thus, using block copolymers it is possible to tailor the order in the electrocatalytic phase, which should improve its behavior.

Usage of supercritical fluids, including $scCO_2$, definitely offers new benefits for synthesis and processing of polymers in general [37] and for electrochemical applications in particular. Indeed, the gas-like absence of any surface-tension-driven effects along with liquid-like density of supercritical fluids make them unique media for processing of different matrices.

Besides, it is a common knowledge, that eventual purity of the materials applied is of a paramount importance for electrochemistry, for both research and production. In this regard, supercritical fluids may also offer certain benefits when applied as media for obtaining or processing electrochemistry-related polymers. Indeed, mainly, these fluids are gases or volatile liquids at normal conditions. Therefore, they leave the modified/synthesized product spontaneously and with high degree of completeness. Thus, the typical problem of a residual solvent is automatically solved. Another consequence is that they are ready to be produced cheaply with a high degree of purity or purified easily after usage. Many